ESTERIFICATION OF OLEIC ACID WITH ETHANOL BY USING TUNGSTATED ZIRCONIA : KINETIC AND MODELING STUDY

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To my beloved family

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ABSTRACT

The esterification of free fatty acids (FFA) mostly found in vegetable oils with ethanol using solid acid catalyst is one of promising method to convert FFA into Fatty Acid Ethyl Ester (FAEE) that is an alternative to replace fossil fuel as energy source mostly in transportation sector. The present study aimed to determine the optimum or best operating condition for the production of FAEE by esterification of oleic acid and ethanol with tungstated zirconia used as solid acid catalyst. Tungstated zirconia used must be activated at 800°C for it functions at the best state by providing most active site for the reaction occur besides providing alternative route that lower than activation energy for reaction to occur. Kinetic model has been developed after the optimum operating condition is determined. From the scope of study, the optimum operating condition of oleic acid esterification can be achieved at 50°C, 1.5 g tungstated zirconia solid catalyst and 5:1 ethanol to oleic acid molar ratio that brings 24.24% oleic acid conversion. Kinetic model used is pseudohomogeneous and from the model, activation energy for esterification which is 9.72 kJ/mol can be determined.

ABSTRAK

Proses pengesteran asid lemak bebas yang biasanya ditemui pada minyak sayuran dengan etanol menggunakan mangkin asid pepejal adalah satu cara yang meyakinkan untuk menukarkan asid lemak kepada Etil Ester Asid Lemak (EEAL) iaitu satu alternatif untuk menggantikan bahan api fosil sebagai sumber tenaga khususnya dalam sektor pengangkutan. Kajian terkini tertumpu kepada mencari keadaan optima atau terbaik untuk penghasilan EEAL melalui pengesteran asid oleik dan etanol dengan tungstated zirconia digunakan sebagai mangkin asid pepejal. Tungstated zirconia mesti diaktifkan pada suhu 800°C untuk berfungsi pada keadaan terbaik bagi menyediakan tapak aktif untuk tindakbalas berlaku di samping menyediakan laluan alternatif yang lebih rendah dari tenaga pengaktifan untuk tindakbalas berlaku. Model kinetik perlu diterbitkan selepas mencapai keadaan optima untuk digunakan dalam proses pengesteran. Daripada skop kajian, dapat dibuktikan keadaan optima pengesteran asid oleik dapat dicapai pada suhu 50°C, 1.5 g tungstated zirconia mangkin pepejal dan 5:1 nisbah molar etanol kepada asid oleik yang membawa kepada 24.24% perubahan asid oleik kepada ester. Model kinetic yang digunakan ialah model homogeneous palsu dan daripada model, tenaga pengaktifan proses pengesteran iaitu 9.72 kJ/mol dapat dikenal pasti.

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LIST OF ABBREVIATIONS/TERMINOLOGY/SYMBOLS

T	-	Temperature
°C	-	Degree Celcius
ml	-	Mililiter
kJ	-	KiloJoule
min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
rpm		Revolutions per minute
M		Molar (mol/dm^3)
FFA	-	Free Fatty Acid
LHHW-		Langmuir-Hinshelwood-Hougen-Watson

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The modernization of today's life has changed the lifestyle of people. People need to move from one place to another to do their job in fast and effective ways. This kind of lifestyle has made a big impact especially in the expansion of transportation industry. Thus, the demands on fuel also increase every year. However, the quantity of fossil fuel is decreased and it is not a renewable source. Thus, we need to find the other sources other than fossil fuel as alternative to fulfill the demands of fuel.

Biodiesel fuel is the new possible alternative to replace the fossil fuel as the energy source especially in transportation sector. This fuel can be produced from esterification of free fatty acid (FFA) and alcohol. Free fatty acids are found easily in vegetable oils or animal fats. The possibility of using vegetable oil as energy source is proposed by Rudolph Diesel in 1892.

The substitution of biodiesel fuel to fossil fuel brings a lot of advantages for consumers. Compared to fossil fuel, the carbon dioxide (CO_2) which emitted from biodiesel would be recovered through the production of biomass (feedstock of biodiesel). It also does not contain sulfur to produce SO_2. The oxygen contained in biodiesel makes it fully combusted and thus the poisonous gas such as carbon monoxide (CO) can be reduced (Park et al., 2008).

The esterification process of free fatty acid with alcohol can be fasten with the presence of catalyst. The catalysts used can be homogeneous or heterogeneous. The homogeneous catalysts such as H_2SO_4 and NaOH are difficult to separate with ester (biodiesel fuel) (Furuta et al., 2006). Thus, these kinds of catalysts are not suitable for the present study. The heterogeneous catalysts that has been used by previous experiments such as Tungstated Zirconia(WO_3/ZrO_2), Amberlyst15, silica-alumina, SAC-13, Sulfated Zirconia, Titania Zirconia, Smopex-101, niobium acid and various zeolites. The solid acid catalyst chosen for the present study is tungstated zirconia.

1.2 Problem Statement

Biodiesel can be the most suitable replacement for the fossil fuel as energy source. Besides of it bring a lot of advantages compared to fossil fuel, the amount of fossil fuel is decreasing every year make it is important to produce biodiesel in a large amount. To produce it in large amount using a new solid acid catalyst, a reactor needs to be designed. Previous studies for biodiesel production do not mention much about the importance of kinetic modeling; therefore the present study will give attention about kinetic and modeling study and develop it.

1.3 Objectives

1) To determine the optimum operating conditions of the esterification of free fatty acid with alcohol selected.

2) To develop the kinetic modeling for the esterification process.

1.4 Scopes of Research

The present study, several important parameters will be investigated. These parameters are temperature, ratio of alcohol to free fatty acid, amount of catalyst used, and presence of triglycerides. The details of the scope are as below:

i) Temperature is between 30-50°C
ii) Amount of catalyst is between 0.5-1.5g
iii) Ratio of alcohol to free fatty acid- 1:1, 3:1, 5:1
iv) Volume of triglycerides is between 10ml, 30ml and 50ml

In this experiment, we will use oleic acid as free fatty acid, ethanol, and tungstated zirconia as the catalyst. Pseudohomogeneous model will be used since it is simple and easy to construct.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is the fuel alternative to petroleum based fuel which is manufactured from vegetable oils or animal fats by catalytically react it with short chain alcohol such as methanol or ethanol. Vegetable oils or animal fats contain many types of free fatty acids. These free fatty acids will react with short chain alcohol to produce biodiesel fuel. This reaction can be accelerated by adding acid or base catalyst. This catalyst however will not affect the yield gain but it just makes the reaction proceeds more quickly.

Biodiesel also can be blended with fossil fuel for use in the retail diesel fuel marketplace. European Union (EU) has started the usage fuel that has been blended with biodiesel since 2005. This blend fuel can be used to vehicle without modifying the engine. The blend fuel is usually labeled by ‘B’ factor. As example, B20 means there is 20% of biodiesel contain in that fuel and B100 means pure biodiesel. Biodiesel can be produced by esterification or transesterification process.

2.2 Transesterification

Transesterification is the process of exchanging the alkoxy group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base. The transesterification reaction will change the chain between alcohol and ester that react. Usually with the presence of triglycerides, transesterification will occur to produce ester and glycerol. Transesterification of triglycerides is shown in Figure 2.1:

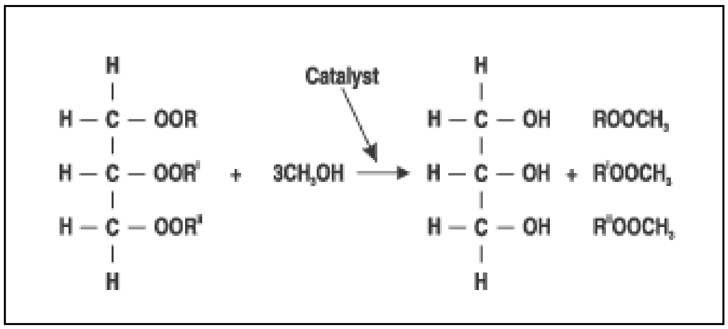

Figure 2.1: Transesterification of triglycerides with methanol to produce 3 molecules of methyl esters and 1 molecule of glycerol.

Transesterification process can be carried out using two methods which are supercritical reaction process and non-catalytic transesterification in bubble column reactor. Vera et al. (2005), has studied the supercritical reaction as shown in Figure 2.2. The term supercritical is used because this reaction has been constructed at temperatures higher than critical temperature of methanol. This reaction used methanol and triglycerides and did not use any of alkaline or acid catalysts. They studied about effect of number of reactor used in the reaction. The findings shows that one-reactor system works with molar ratio methanol: oil=42 and pressure needed is 14-43MPa but when two reactor system is applied, the molar ratio methanol: oil=10 and pressure needed is only 4MPa.

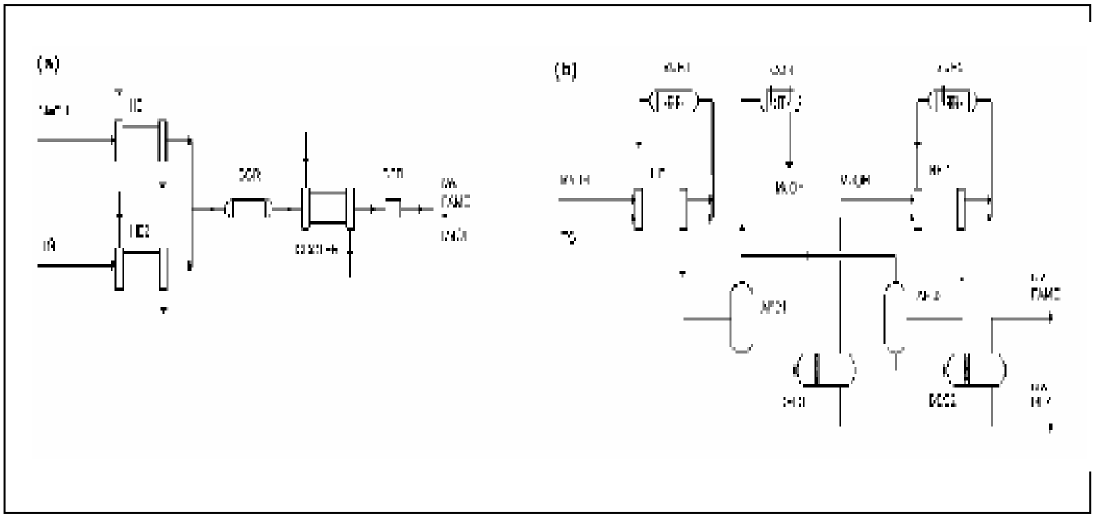

Figure 2.2: Experiment setup for supercritical reaction of transesterification.

Joelianingsih et al. (2007) has studied about non-catalytic transesterification in bubble column reactor. The reactants used are palm oil with superheated methanol. The study has been carried out at 523-563 K reactor temperature under atmospheric pressure. They found out that in the transesterification, the methyl ester content in the reaction product decreased as the reaction temperature was increased. At T=523 K, the methyl ester content is highest which is 95.17% w/w. Figure 2.3 shows the schematic flow diagram of reactor used in non-catalytic transesterification experiment.

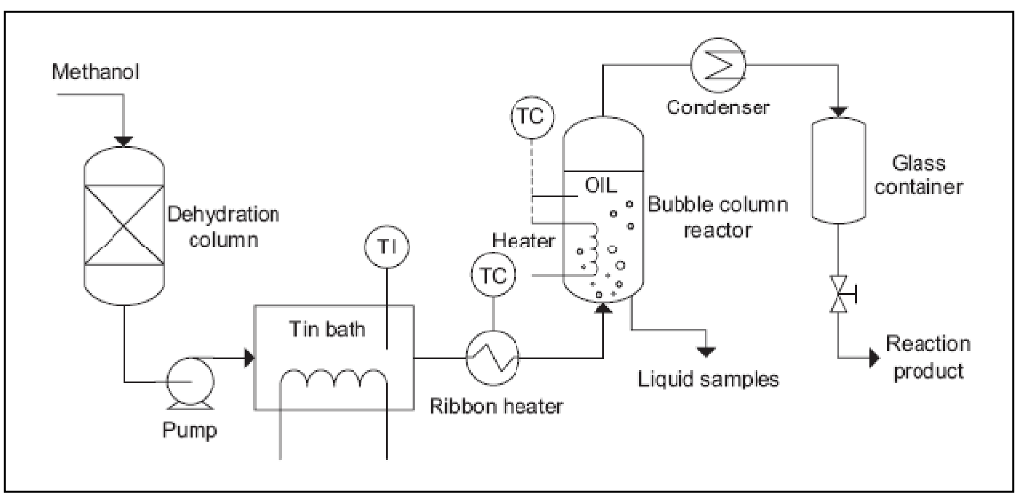

Figure 2.3: Experiment setup for non-catalytic transesterification through bubble column reactor

2.3 Esterification

Esterification process is reaction between acids such as carboxylic acid or free fatty acid with alcohol to produce ester and water. To produce biodiesel fuel, fatty acids will react with short chain alcohol to produce biodiesel fuel and water.

Lopez et al. (2008), has studied about the esterification of free fatty acid with ethanol. The free fatty acid used is caprylic acid and the study is about to determine the effect of three different solid acid catalysts in esterification process. Three different solid acid catalysts that has been used are sulfated zirconia, tungstated zirconia and titania zirconia. The study shows that sulfated zirconia catalyst was found to be the most active for this reaction. However, its activity was not easily regenerated. Compared to titania zirconia, tungstated zirconia has greater activity in esterification and it is easier to regenerate compare to sulfated zirconia by re-calcination in air. Thus, they conclude that tungstated zirconia catalyst is most suitable catalyst in esterification process of free fatty acid. The reaction of esterification is shown in Figure 2.4:

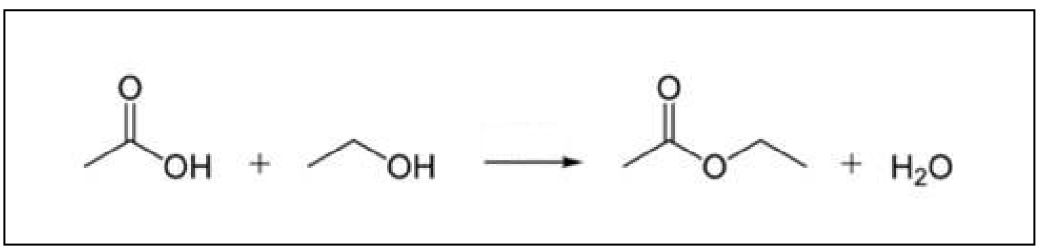

Figure 2.4: Esterification of free fatty acid with ethanol to produce ethyl ester and water.

Esterification can be carried by two methods, which is batch reaction and continuous reaction by using packed bed reactor. In batch reaction, powder-type catalyst is used since it has higher surface area compare to pellet-type catalyst. However, pellet-type is more suitable for packed bed reactor because of the possible loss of catalyst and pressure drop with the powder-type catalyst. The continuous reaction has advantage in mass production; however the conversion of FFA is might be lower than batch reaction.

Thus, the optimization of pellet-size catalyst is very important in order to maximize the activity of catalyst and make the conversion of FFA to be exact with batch reaction. (Park et al., 2008).

Figure 2.5 shows the experimental setup for batch reactor made by Ni and Meunier (2007). Batch reactor needs to be fixed in operation time to analyze the sample and to observe the difference in conversion when the operation conditions are vary. However, in order to produce biodiesel fuel in a large amount, batch reaction is not very suitable because it takes longer time period and space area used is relatively high compared to continuous reaction process.

Figure 2.6 shows the packed bed reactor for continuous production of biodiesel made by Park et. al (2008). Packed bed reactor is suitable for the industrial production of biodiesel to produce a very large amount to fulfill consumer demand.

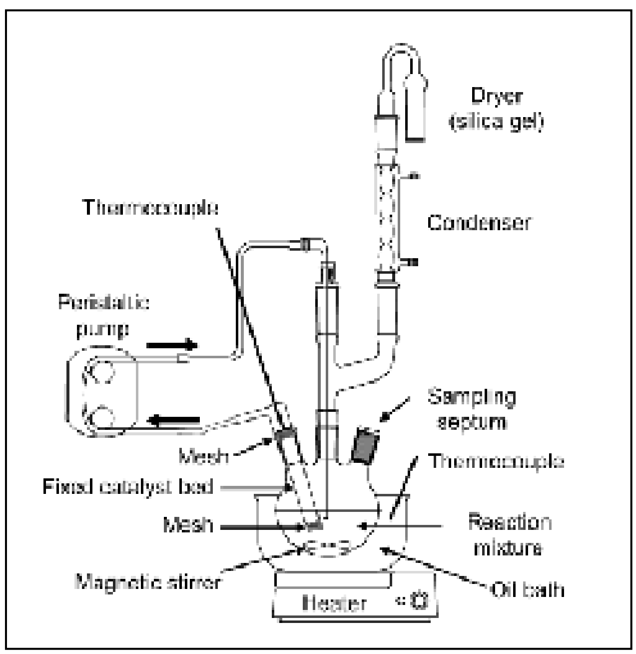

Figure 2.5: Schematic layout of the reactor system used for the experiments involving the recirculation of the reaction mixture through a fixed catalytic bed.

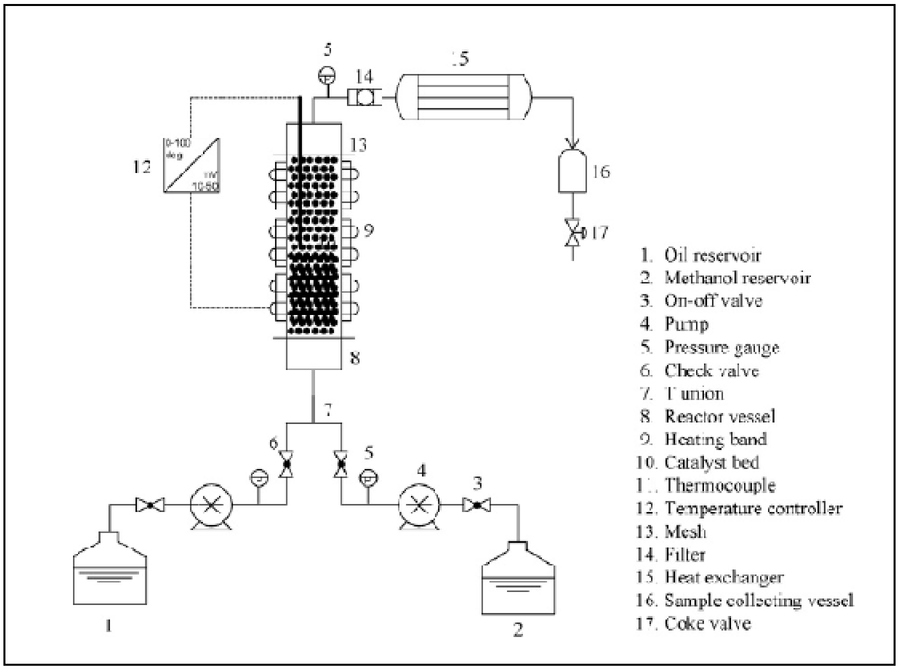

Figure 2.6: Schematic layout of the packed bed reactor for the continuous production of biodiesel.

2.4 Homogeneous Catalytic Esterification

Esterification of free fatty acid can be homogeneously or heterogeneously catalyzed. Marchetti and Errazu (2008) used homogeneous catalyst for the reaction of oleic acid with methanol. This study was carried out in the presence of triglycerides which is sunflower oil. The catalyst used is sulfuric acid (H_2SO_4). This study is about to determine the conversion of FFA when temperature, amount of alcohol, amount of catalyst and amount of initial FFA used are vary. The amount of catalyst used only affect the time of conversion. However, the final conversion is still the same between different amounts of catalyst used. When molar ratio was varied, the amount of alcohol affects the reaction. When the amount of alcohol is higher, the rate of reaction became slower but it reaches higher conversion of FFA. This reaction however, is hard to separate the catalyst from the product since it is miscible in the product. It has affected the yield gain and the purity of the product will become lower.

2.5 Heterogeneous Catalytic Esterification

Heterogeneous catalytic esterification is esterification which is using solid catalyst and the catalyst is not miscible in the reaction mixture. Park et al. (2008) studied the effect of various types of solid acid catalysts on the biodiesel production by varying the heterogeneous catalyst in the reaction. The solid catalysts used in the experiment are sulfated zirconia (SO_4^{2-}/ZrO_2), SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2, H-zeolite, Cs-heteropoly acid and tungstated zirconia(WO_3/ZrO_2). The finding shows that in biodiesel production, sulfated zirconia and tungstated zirconia are the suitable solid acid catalysts. However, sulfated zirconia is not selected because of the potential loss of SO_4^{2-} in its liquid phase application. Tungstated zirconia is the most suitable solid acid catalyst because it can be used for the long reaction. The result showed that 65% conversion could be maintained for up to 140 hours. Besides, the activity of this catalyst is easily regenerated through a simple air-calcination. The calcinations of tungstated zirconia is carried out by heat it in oven at 130°C for one hour, cooled to room temperature then the heating process continue at 800°C for one hour in furnace (Furuta et al. 2006)

Table 2.1 shows the past studies of biodiesel production via esterification and transesterification process using homogeneous and heterogeneous catalyst.

Table 2.1: Summary of esterification and transesterification process from previous studies.

Reaction	Catalyst	Findings	Author
Transesterification of soybean oil with methanol and esterification of n-octanoic acid with methanol	Titanium-, aluminium-, and potassium-doped zirconia	Titanium- and aluminium-doped zirconias are promising solid acid catalysts for both reaction	Furuta et. al. (2005)
Transesterification of used vegetable oils with methanol	H-zeolite, SO_4^{2-}/ZrO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2 and WO_3/ZrO_2	Tungstated zirconia, WO_3/ZrO_2 is the most suitable due to its high activity and stability	Y.-M. Park et al. (2008)
Esterification of oleic acid with refined sunflower oil with ethanol when operating condition varies	Sulfuric acid (H_2SO_4)	Rate of reaction increases when amount of catalyst and temperature increase. Conversion increases when amount of FFA and alcohol increase	Marchetti and Errazu (2008)
Esterification of oleic acid with methanol in the presence of triglycerides, kinetic studies	Ion-exchange sulfonic resin	Pseudohomogeneous second-order model have been determined by nonlinear regression	Tesser et al. (2005)
Esterification of a decanoic acid with methanol by reactive distillation	Amberlyst 15	Pseudohomogeneous kinetic model is not able to describe the experimental results and Langmuir – Hinshelwood – Hougen – Watson (LHHW) is derived.	Steinigeweg and Gmehling (2003)
Esterification of palmitic acid with methanol in sunflower oil using batch and fixed bed reactor	SAC-13 (Nafion/SiO_2), SAC-13 and sulfated zirconia	SAC-13 appeared as most promising catalyst	Ni and Meunier (2007)
Esterification of dodecanoic acid with 2-ethylhexanol by reactive distillation	Sulfated zirconia	Sulfated zirconia is suitable for the synthesis of 2-ethylhexyl dodecanoate by reactive distillation	Omota et al (2003)